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NRL Report 6047

Filament-Winding Plastics

Part 1 - Molecular Structure and Tensile Properties

J. R. GRIFFITH AND F. S. WHISENHUNT, JR.

Organic and Biological Chemistry Branch
Chemistry Division

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U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

ABSTRACT

Filament winding is a process by which strands of material (glass fibers) are treated with a liquid resin and accurately placed upon a mandrel to form a structure. The resin hardens into a plastic, and the structure becomes rigid as this process occurs. Epoxide resins and aromatic diamine curing agents have been extensively used in this application.

The physical properties of a filament-winding plastic are dependent upon the molecular characteristics of the resin and its curing agent. When the diglycidyl ether of bisphenol-A reacts with m-phenylene diamine, the resulting plastic strongly binds glass filaments, and good quality filament-wound objects may be produced from these materials.

Two additional plastics which are suitable for this application have been produced from curing agents which are molecularly similar to m-phenylene diamine. One of these curing agents, m-aminobenzylamine, has one aliphatic amino group, and the other, m-xylylene diamine, has two aliphatic amino groups. Tensile and elongation properties are compared for the plastics produced from these amines and the diglycidyl ether of bisphenol-A. The plastic produced from m-aminobenzylamine has outstanding properties and pressure vessels produced using it are believed to be superior to those containing m-phenylene diamine.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem R05-24C
Project SPO WW-041

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FILAMENT-WINDING PLASTICS

PART 1 - MOLECULAR STRUCTURE AND TENSILE PROPERTIES

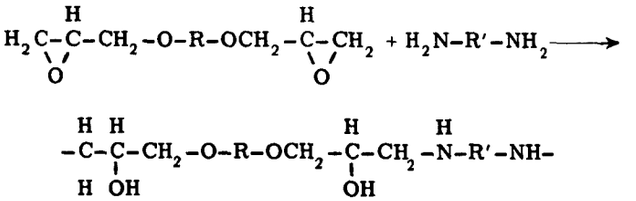
INTRODUCTION

Filament winding is the process of producing lightweight, strong structures by the accurate placement of strands of material, usually glass fibers impregnated with a resinous binder, upon a mandrel of suitable shape, following which the composite is cured to form a reinforced plastic. A filament-winding resin is, in a broad sense, any adhesive system which is capable of binding threadlike units of material to form a wound structure. Maximum development of the current state of the art has been accomplished with resins of the epoxy class. In one major application of the filament-winding process–rocket motor case production–epoxide resins are used almost exclusively. These resins are available in liquid form, and thus are easy to apply to glass fibers before or during the winding process; they may be readily converted to tough plastics at controlled rates, and they yield structures which are tough and durable.

High performance rocket motor cases, such as those used in the A-3 Polaris, contain at least 70% glass by weight and may contain over 80% glass by weight. Since glass fiber has a tensile strength approximately thirty times as great as that of the binder plastic, it is obvious that glass is the primary strength-giving component of the motor case. Therefore the plastic plays a secondary but significant role as far as the strength of such a structure is concerned.

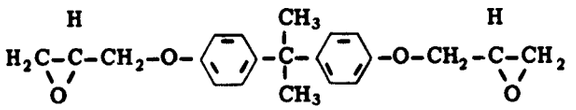
AMINE-CURED EPOXIDE FILAMENT-WINDING PLASTICS

The amine-cured epoxide plastics are actually polyaminoethers with pendant hydroxyl groups along the molecular chains. The basic polymerization reaction may be illustrated as follows:



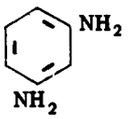
Thus, the structural properties of the cured epoxide plastics depend upon the molecular structure of the amine unit as well as the structure of the epoxide unit.

An epoxide resin which has received extensive use in filament-winding processes is the diglycidylether of bisphenol-A:



Because the material is not expensive, melts at low temperature, can be cured with good degree of control, and produces tough plastics, it has been of key importance in the industry.

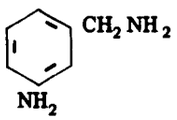
The most frequently used amine coreactant has been m-phenylene diamine:



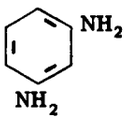
At normal temperatures the epoxide resin reacts slowly with the amine, reaching only a "B"-stage cure (i.e., a semicured state) over many hours. However, complete cure in a few hours can be accomplished at elevated temperature (usually at about 300°F). These are very convenient fabrication and processing characteristics. This system has been used by this Laboratory as a reference standard in filament-winding plastics studies.

MOLECULAR MODIFICATIONS OF THE STANDARD AMINE

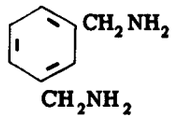
Because of the generally good properties of the standard epoxide system, it was thought that profit would ensue from a study of the effects of slight molecular modifications of the standard amine. Three molecular analogs, m-aminobenzylamine, m-xylylene diamine, and m-phenylene diamine (the standard) were obtained, the former by synthesis, and the latter two from a commercial source.



m-aminobenzylamine



m-phenylene diamine



m-xylylene diamine

At room temperature, m-xylylene diamine is a liquid, and m-aminobenzylamine is a waxy solid which melts about 40°C. When used in conjunction with the standard epoxide resin, both produce liquid systems in the precured state, suitable for filament winding. They are somewhat more reactive than m-phenylene diamine; however, winding operations with sizeable quantities (400 to 500 grams) have been performed at NRL without difficulty. Both systems produce plastic which are nearly water-white and are very attractive in appearance, both m-xylylene diamine and the resin containing it have a tendency to cloud, as the amine absorbs carbon dioxide from the atmosphere.

TENSILE PROPERTIES OF THE CURED PLASTICS

The standard resin was reacted with each of the three amines in stoichiometric ratios to produce flat sheets of plastic from which tensile samples (dumbbells) could be cut. All of the systems were "B"-stage cured for 12 hours at 72°F, and precured at 150°F for

1 hour. A temperature of 300°F for 3 hours was required to thoroughly cure the standard system, but each of the other more reactive systems were cured at 250°F in 3 hours. Tensile properties of accurately machined and polished tensile dumbbells were obtained by the use of an automatic tensile testing machine at a crosshead speed of 0.05 inch per minute in accordance with ASTM method D638-60T.* Table 1 gives the result of maximum tensile, modulus, and elongation to break for five samples of each plastic.

These plastics do not have a sharp yield point. Figure 1 shows typical stress-strain curves (to rupture) of tensile specimens designed to compare the three types of curing agents used in this study. It is to be noted that the specimens produced from m-phenylene diamine and m-xylylene diamine ruptured while the stress-strain curve was still sloping sharply upward. However, the specimens from m-aminobenzylamine passed through a distinct maximum in the tensile-elongation curve and had taken a slightly negative slope before rupture occurred at a greater elongation than that of the other two specimens. It is obvious that the m-aminobenzylamine sample absorbed considerably more energy before rupture than did the other two specimens. It is believed that this type of resin performance will tend to minimize craze cracking in filament-wound internally pressurized structures, and prove superior to the performance of the standard resin and curing agent system now in general use.

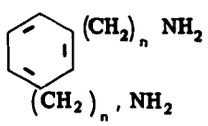
DISCUSSION

Many difficulties are encountered in an effort to attribute a change in the physical strength of a filament-wound structure to a change in a property of the resin system used in the winding process. It is thought by some investigators that an increase in ductility of the binder plastic will produce a stronger, more durable composite. Most of the usual chemical methods for increasing the elongation of a resin cause a substantial decrease in tensile strength and modulus. Consequently, the more extensible plastic is, in fact, weaker. Since the binder plastic is a force-transfer medium until it ruptures, more ductile stronger resin systems are needed for rocket motor case construction.

The tensile strength of the plastic produced from m-aminobenzylamine is approximately the same as that of the standard plastic. However, it has considerably greater elongation than the standard plastic (10.5% versus 7.5%). The modulus of the standard plastic is greater by approximately 12%. In spite of the decreased modulus, the m-aminobenzylamine system produces composite structures which are believed to be stronger than the ones produced with the standard plastic. The production of pressure bottles designed to test this belief is now in progress, and preliminary data indicate that higher burst levels can be obtained by use of the m-aminobenzylamine system.

FUTURE WORK

The amine curing agents under study are of a homologous series of the general formula:



*"Tensile Properties of Plastics," ASTM Method D638-60T in ASTM Standards on Plastics, Twelfth Edition, Philadelphia:American Society of Testing Materials; March 1961.

Table 1
Tensile Properties of Amine-Cured Epoxide Plastics

Sample	m-Phenylene Diamine			m-Xylylene Diamine			m-Aminobenzylamine		
	Tensile (psi)	Elongation (percent)	Elastic Modulus (psi)	Tensile (psi)	Elongation (percent)	Elastic Modulus (psi)	Tensile (psi)	Elongation (percent)	Elastic Modulus (psi)
1	12,900	7.5	427,000	10,800	7.4	410,000	12,300	11.0	426,000
2	12,600	6.8	451,000	10,800	7.8	427,000	12,200	10.3	403,000
3	12,400	6.3	488,000	10,000	4.9	433,000	12,200	10.0	402,000
4	13,000	8.7	451,000	10,800	7.6	445,000	12,100	11.5	410,000
5	12,900	8.1	496,000	10,400	5.6	464,000	12,100	9.5	406,000
Average	12,800	7.5	463,000	10,600	6.7	436,000	12,200	10.5	409,000
Standard Deviation	200		28,000	360		20,400	<100		9,700

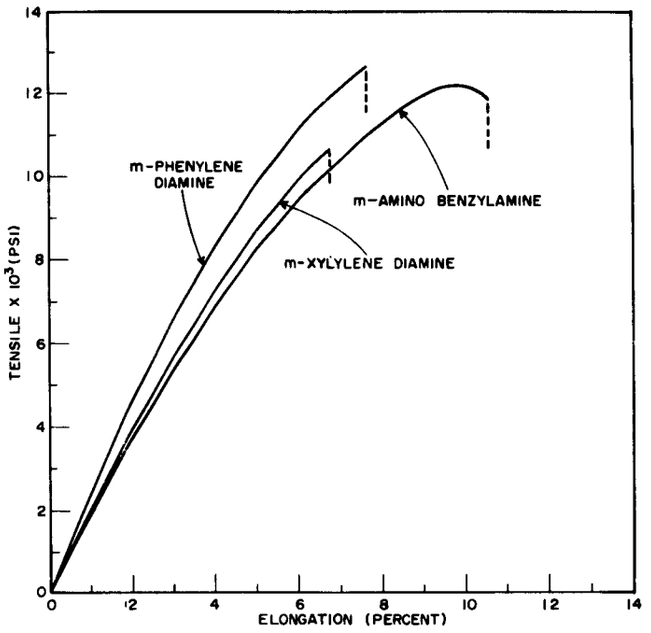


Fig. 1 – Tensile-elongation curves of amine-cured epoxide plastics

The parent substance is m-phenylene diamine for which n = 0 and n ′ = 0. The formula for m-aminobenzylamine is obtained when n = 1 and n ′ = 0, and that for m-xylylene diamine is obtained when n = 1 and n ′ = 1. Other members of the series are being synthesized, and the plastics produced from them will be evaluated with respect to tensile properties, winding suitability, and composite properties.

ACKNOWLEDGMENT

Mr. A. G. Sands and Mr. R. C. Clark prepared the tensile specimens and obtained the data.

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Naval Research Laboratory. Report 6047. FILAMENT-WINDING PLASTICS. PART 1.– MOLECULAR STRUCTURE AND TENSILE PROPERTIES, by J. R. Griffith and F. S. Whisenhunt, Jr. 5 pp. and figs., March 16, 1964.

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The physical properties of a filament-winding plastic are dependent upon the molecular characteristics of

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1. Filament – Wound construction – Materials
2. Resins – Molecular structure
3. Resins – Tensile prop.

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